THE BEHAVIOR OF α-THIAKETONES AND α-AMINOKETONES UNDER CONDITIONS OF THE CLEMMENSEN REDUCTION AND ELECTROLYTIC REDUCTION

BY

JOHN FIGUERAS

B.S., University of Rochester, 1949
M.S., University of Illinois, 1950

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
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PART I

The Cleavage of α-Aminoketones During Electrolysis

Previous work in these laboratories (1) showed that the reduction of 1-methyl-2-ethyl-3-piperidone at a lead cathode at 60° yielded methylheptylamine. Di-*n*-butylamine was obtained from 1-*n*-butyl-3-pyrrolidone under the same conditions. On the basis of these results, it was anticipated that the electrolytic reduction at a lead cathode at 60° of bicyclic *alpha*-aminoketones should yield medium-sized rings having a hetero-nitrogen atom.

The electrolysis of 1-ketoquinolizidine under the specified conditions gave an aminoalcohol in 59% yield. Dehydration of this aminoalcohol, followed by hydrogenation, gave azacyclodecane, characterized by comparison of its picrate with an authentic sample (2). The infrared absorption spectrum and analytical data were consistent with the proposed structure for the aminoalcohol: 5-hydroxyazacyclodecane. No evidence for the position of the hydroxyl group was obtained, but previous work (1) has shown that rearrangements with respect to the position of the hydroxyl group are not to be expected.

In a similar fashion, 4-hydroxyazacyclononane was obtained in 49% yield by the electrolysis of 1-ketoöctahydropyrrocoline. Infrared and analytical data supported this structure. Attempts to remove the hydroxyl group in order to demonstrate the nature of the basic skeleton of the molecule failed in this instance. However, the facile methylation of the aminoalcohol by formaldehyde-formic acid revealed the presence of an -NH group. The infrared absorption spectrum of the

methylated product showed the presence of a methyl group and the retention of the hydroxyl group, thus establishing the proposed structure as correct.

PART II

The Rearrangement of α-Thiaketones During Clemmensen Reduction (3)

The rearrangement of *alpha*-aminoketones during Clemmensen reduction has become a well-established fact (4). Although von Braun (5) obtained the rearranged product, 1-methyl-1,2-dihydroisothionaphthene, from a Clemmensen reduction of 4-isothiochromanone, it was desired to apply the reaction to thiaketones which were more closely analogous to the *alpha*-aminoketones which had been studied to date.

3-Ketothiacyclohexane was prepared by the alkylation of ethyl sodio-thioglycolate with ethyl γ-chlorobutyrate, followed by Dieckmann cyclization, hydrolysis and decarboxylation. 3-Ketothiacycloheptane was prepared in an analogous manner, starting with ethyl δ-chlorovalerate. The Clemmensen reduction of 3-ketothiacyclohexane gave 2-methylthiacyclopentane (21% yield), identified by comparison of its infrared absorption spectrum with that of an authentic sample. Similarly, 2-methylthiacyclohexane (34% yield of crude product) was obtained from the Clemmensen reduction of 3-ketothiacycloheptane. The Clemmensen product was again identified by comparison of its infrared absorption spectrum with that of an authentic sample. The authentic samples of cyclic sulfides required for this work were prepared by condensation of the appropriate dihalides with sodium sulfide.

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VITA

The author was born on October 28, 1924, in Rochester, New York. After completing his primary and secondary education in the public schools of Rochester, he began studies at the University of Rochester in 1942. In 1943 he was called into the Army and served in France, Germany, the Philippines and Japan. After his discharge from the Army in 1946, he finished his undergraduate education at the University of Rochester, and received the Bachelor of Science degree in 1949. He enrolled in the Graduate School of the University of Illinois in February, 1949. The author was granted a Master of Science degree in 1950 by the University of Illinois. He is a member of Phi Beta Kappa, Sigma Xi, Phi Lambda Upsilon and Alpha Chi Sigma.